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Radian Corp., Research Triangle Park, NC

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Capt. Richard A. Ashworth
Hq AFESC/RDVW
Tyndall Air Force Base, FL 32403

Michael A. Palazzolo
Radian Corporation
Research Triangle Park, NC 27709

Bruce A. Tichenor
Air and Energy Engineering Research Laboratory
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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EPA Project Officer
Bruce A. Tichenor

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT The paper discusses the effectiveness of two catalytic systems in destroying specific organic compounds (jet fuel components, chlorinated solvents). (NOTE: Catalytic incineration is used to destroy volatile organic compounds contained in air emissions from a variety of industrial processes.) The test vapor streams consisted of low concentrations (3 to 200 ppmv) of mixtures which represented emissions from air strippers used to treat contaminated groundwater at U.S. Air Force bases. One system employed a metal oxide catalyst in a fluidized bed. The other system used a fixed-bed proprietary catalyst, supplemented with UV light and ozone injection. Destruction efficiencies for the fluidized-bed reactor were between 97 and 99% at sufficiently high catalyst temperatures (500 C). Mixture composition, air-to-gas ratio, and space velocity affected destruction efficiency minimally. Destruction efficiencies for the UV-catalytic oxidizer ranged from 16 to 67% without ozone addition. With ozone, complete oxidation of the text mixture components was achieved, but high concentrations of several unidentified reaction products was observed.

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Volatilization	Strippers	Catalytic Oxidation	20M	13I, 07A
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DESTRUCTION OF ORGANIC CONTAMINANTS BY CATALYTIC OXIDATION

Capt. Richard A. Ashworth
HQ AFESC/RDVW
Tyndall Air Force Base, FL 32403
(904) 283-4628

Michael A. Palazzolo
Radian Corporation
PO Box 13000
Research Triangle Park, NC 27709
(919) 541-9100

Bruce A. Tichenor
U.S. EPA, AEERL, MD-54
Indoor Air Branch
Research Triangle Park, NC 27711
(919) 541-2991

Abstract - Catalytic incineration is used to destroy volatile organic compounds (VOCs) contained in air emissions from a variety of industrial processes. We investigated the effectiveness of two catalytic systems in destroying specific organic compounds (jet fuel components, chlorinated solvents). The test vapor streams consisted of low concentrations (3 to 200 ppmv) of mixtures which represented emissions from air strippers used to treat contaminated groundwater at U.S. Air Force bases. One system employed a metal oxide catalyst in a fluidized-bed configuration. The other system used a fixed-bed proprietary catalyst, supplemented with UV light and ozone injection. Destruction efficiencies for the fluidized-bed reactor were between 97 and 99% at sufficiently high catalyst temperatures (950°F)*. Mixture composition, air-to-gas ratio, and space velocity affected destruction efficiency minimally. Destruction efficiencies for the UV-catalytic oxidizer ranged from 16 to 67% without ozone addition. With ozone, complete oxidation of the test mixture components was achieved, but high concentrations of several identified reaction products were observed.

INTRODUCTION

Groundwater contaminated with volatile organic compounds (VOCs) resulting from spills, leaking storage tanks, and past disposal of jet fuel and chlorinated solvents is a pressing environmental problem at numerous Air Force bases. For this reason, we are developing techniques to clean up groundwater contaminated with VOCs. Packed column air stripping has proven to be a cost-effective and efficient method for removing VOCs from groundwater, but it has been criticized by numerous environmental regulatory agencies because of potential air pollution. To address this concern, we

(*) Metric equivalents are listed at the end of the paper for readers more familiar with that system.

have tested the effectiveness of catalytic oxidation for destroying the VOCs in the air streams, enabling us to use air stripping in situations where it might otherwise be banned.

Catalytic oxidation is a combustion process in which the VOC-laden air stream is preheated and passed through a catalyst bed usually containing metal oxides or noble metals. The catalyst allows the oxidation to occur rapidly and at lower temperatures than required for thermal incineration. Catalytic oxidations occur in the temperature range 700-900°F whereas thermal incineration requires temperatures between 1300 and 1500°F (Shareef et al., 1984). This reduced temperature requirement translates to a potential cost advantage for catalytic systems.

Catalytic oxidation is commonly used in industrial operations to control nonchlorinated compounds such as olefins, aromatics, and oxygen- or nitrogen-containing compounds (Shareef et al., 1984). In most of these operations the gas stream contains only a few compounds at high concentrations (1,000-25,000 ppm). Before the technique can be applied to groundwater air stripping operations, performance data are needed on gas streams containing chlorinated organic mixtures at relatively low concentrations (<200 ppm). In the first phase of our research we evaluated the effectiveness of commerically available pilot-scale catalytic oxidizers.

We tested the oxidizers for their ability to destroy a mixture of chlorinated organics and hydrocarbons over a wide range of operating conditions. Our objective was to determine if the techniques would be effective in treating gas streams from air strippers used in groundwater cleanup. Prior to initiating the testing program, we contacted major vendors of catalytic systems to: (1) determine availability of catalysts and catalytic systems suitable for destroying chlorinated organic/hydrocarbon mixtures, and (2) identify vendors with existing laboratory or pilot-scale units that could be tested under this program. We identified two systems suitable for evaluation.

EXPERIMENTAL

Description of Systems

A 500 scfm fluidized-bed catalytic incinerator leased from ARI International, Palatine, IL, contained spherical pellets of aluminum oxide coated with a proprietary metal oxide catalyst (Figure 1). Air spiked with the test compounds was blown into the unit by a 500 scfm inlet blower. The gases entered the preheater section and were heated to the desired catalyst inlet temperature. Test compounds were oxidized on the fluidized catalyst, and exhaust gas was vented through the stack. A separate blower supplied air for the natural gas burner. The system had a non-fluidized catalyst volume of 2.85 ft^3, which resulted in a space velocity of 10,500 hr^{-1} at 500 scfm. The fluidized-bed volume and bed depth were approximately 5 ft^3 and 16 in., respectively.

A 20 scfm ultraviolet (UV)-oxidizer was leased from Ultrox International, Culver City, CA. The UV test unit was part of a complete pilot-scale water treatment system that consisted of an ozone generator, a water-phase UV reaction tank, and a gas-phase UV-catalytic reactor (Figure 2). Only the gas-phase reactor was tested during this program.

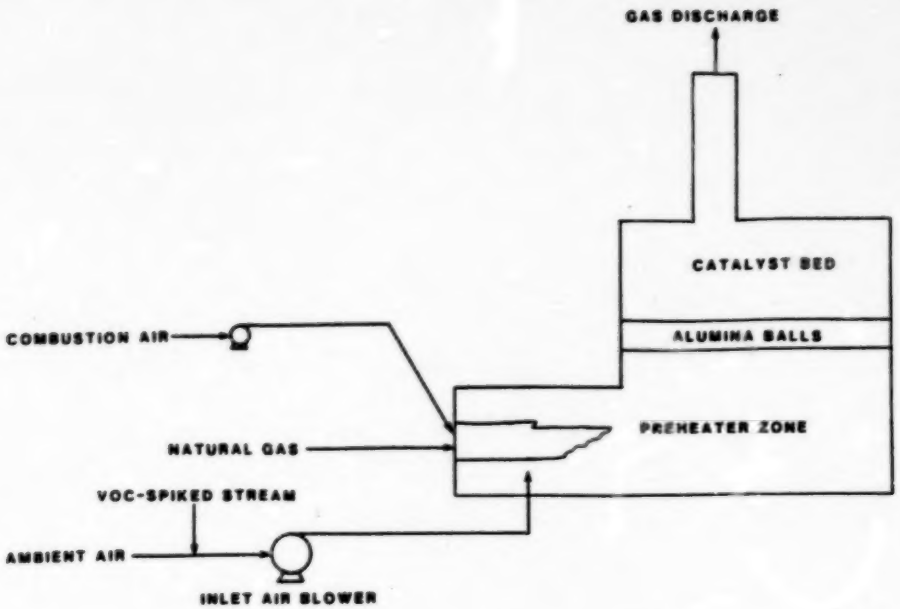

Figure 1. Fluidized-Bed Catalytic Incinerator.

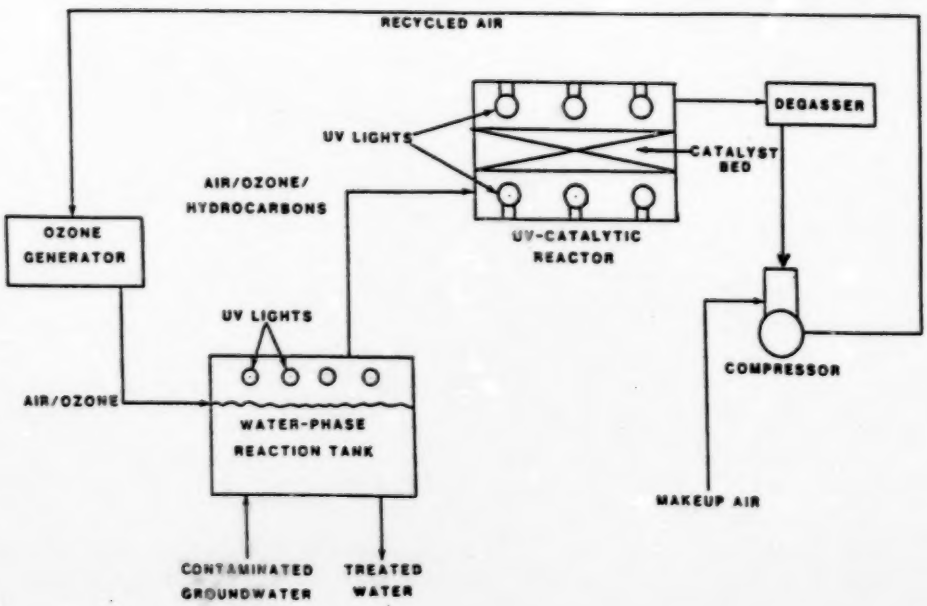

Figure 2. UV-Catalytic Test System

Contaminated air was passed through the gas-phase reactor to determine destruction efficiencies. The air streams entered the UV-catalytic reactor at the connection between the UV-catalytic reactor and the water-phase reaction tank. The reactor contained UV lamps and a proprietary heterogeneous catalyst. The UV-catalytic reactor operated at ambient temperatures (70 to 100°F), and heat generated by the UV lamps was removed by a pre-cooled stream of air or nitrogen. The reported reactor design flow rate was 10 to 20 scfm, with an effective fixed-bed volume of 0.3 ft^3 and a space velocity of 3000 hr^{-1} at 15 acfm.

Experimental Design

The hydrocarbon mixtures selected for testing were representative of gases released from Air Force air stripping operations. The compounds and concentrations studied are shown in Table 1. The target concentrations were obtained by metered liquid injection of the study compounds into a heated ambient air line (Figure 1). After the liquid flash vaporized, the gas passed through a mixing chamber.

Table 1. Mixture Compositions and Target Concentrations for Catalytic Oxidation Tests

Mixture No.	Compounds	Inlet Concentrations ppmv
1	Trichloroethylene	1.9-6.3
	1,2-dichloroethylene	1.0-8.5
2	Trichloroethylene	2.7
	Benzene	1.5
	Ethylbenzene	5.6
	Pentane	11.5
	Cyclohexane	14.1
3	Vinyl Chloride	7.5
	Trichloroethylene	1.8
4	1,2-dichloroethane	10-50
	Trichloroethylene	10-50
	1,1,2-trichloroethane	10-50
	Tetrachloroethylene	10-50

Major operating parameters for each catalytic unit were varied throughout the evaluation. The fluidized-bed testing was generally conducted to characterize destruction across the gas-fired preheater and catalyst bed as a "system." However, heater and catalyst destruction efficiencies were also determined separately at most test conditions.

Concentrations of VOCs were measured by gas chromatography as described in EPA Method 18 (40 CFR part 60). Gas samples with concentrations less than 1 ppmv were sampled using the volatile organic

sampling train (VOST). Samples from inlet, preheater, and outlet were analyzed while test conditions were held constant. Three inlet gas samples were analyzed first. Three outlet gas samples, followed by one additional inlet sample, three preheater samples (if applicable), and one final inlet sample were then analyzed. This approach gave sufficient system inlet data to verify that the spiking additions were constant throughout the test run.

A Shimadzu 6AM gas chromatograph with a flame ionization detector was used for VOC analysis. A six-port gas sampling valve with a 5 ml stainless steel heated sample loop was used. Gas samples were blown through the sample loop at a constant rate. The chromatographic separations were done with a 6 ft x 1/8 in. stainless steel column packed with 1% SP-1000 on 60/80 mesh Carbopack B. Each day the GC/FID was calibrated with certified (±2%) compound specific calibration gases.

RESULTS AND DISCUSSION

Fluidized Bed Reactor

Effect of Temperature and Space Velocity

Both temperature and space velocity markedly affect destruction efficiency, and they also have a major influence on system economics. The most economical unit would be the one operating at the lowest temperature and highest space velocity while achieving the desired destruction efficiency. Destruction efficiency is a strong function of temperature and a weak function of space velocity (Figures 3 and 4). However, the range of space velocities (7,000 to 10,500 hr^{-1}) was narrow due to the requirement for maintaining a fluidized bed without losing catalyst material. The highest destruction efficiency was observed at the lowest space velocity (highest residence time), 7,000 hr^{-1}. This effect was consistent for each mixture, but the increase in destruction efficiency was never over 4%.

System destruction efficiency is based on the destruction of the compound in both the preheater and the catalyst bed. Therefore, samples were collected before and after the preheater and catalyst bed to measure the destruction in each section. The preheater destruction efficiencies generally ranged from 20 to 60%, and thus contributed substantially to the overall destruction efficiency under most test conditions. This finding suggests that catalytic incinerator performance may be improved by preheater designs that optimize contact between the inlet gas stream and the flame zone. The effect that this improved destruction in the preheater may have on the formation of products of incomplete oxidation is not known.

Effects of Chemical Structure on Oxidation

The compounds most easily destroyed by the fluidized-bed catalytic system were cyclohexane, ethylbenzene, and pentane (Figure 5). Benzene and tetrachloroethylene were the most difficult to destroy. Chlorinated compounds were readily destroyed (efficiency greater than 90%), but temperatures greater than 900°F were required (Figure 6).

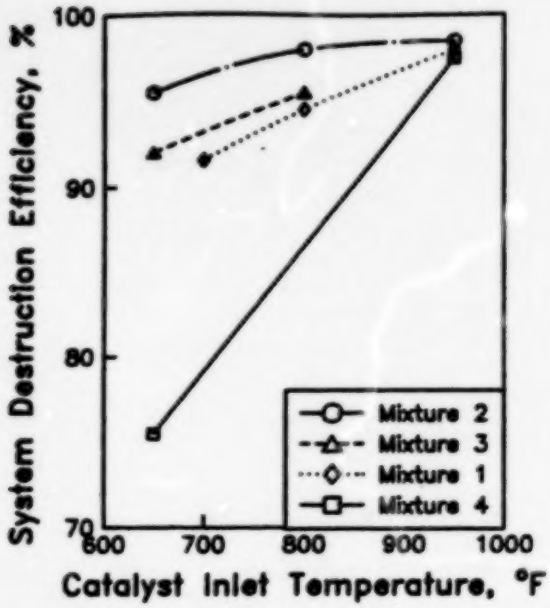

Figure 3. Destruction Efficiencies as a Function of Temperature at a Space Velocity of 7,000 hr^{-1}.

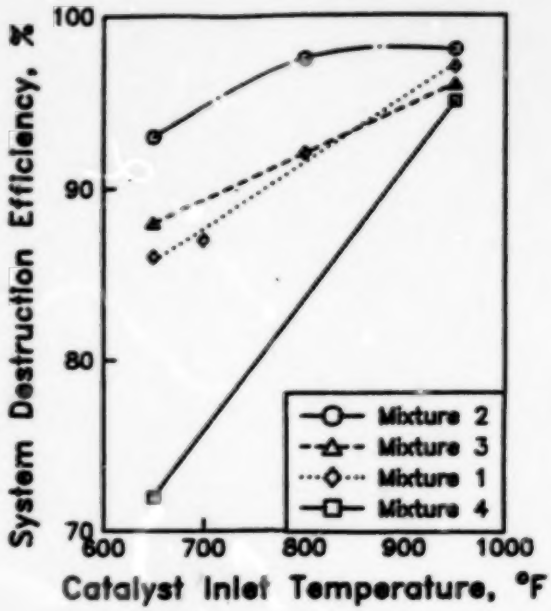

Figure 4. Destruction Efficiencies as a Function of Temperature at a Space Velocity of 10,500 hr^{-1}.

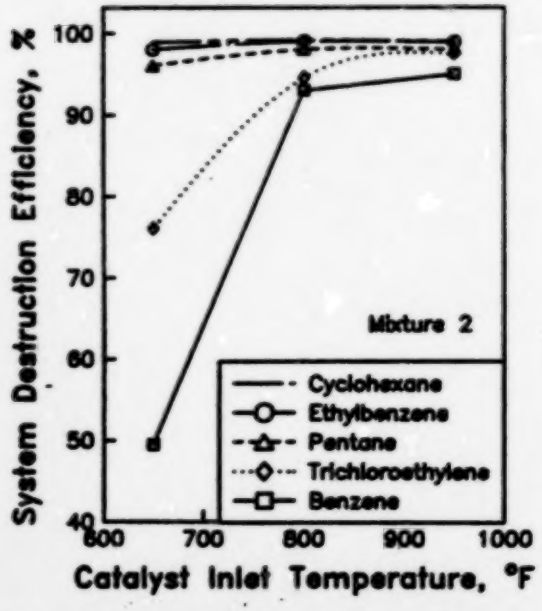

Figure 5. Destruction Efficiencies as a Function of Temperature at a Space Velocity of 10,500 hr^{-1}.

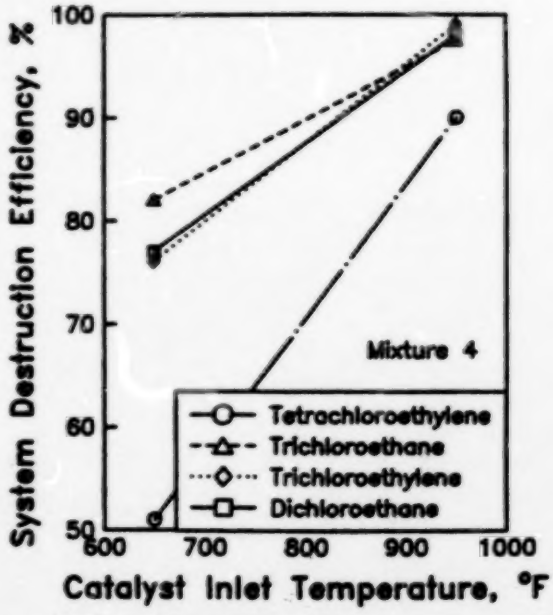

Figure 6. Destruction Efficiencies as a Function of Temperature at a Space Velocity of 10,500 hr^{-1}.

Mixture Effects

Mixture interactions can be an important consideration in the selection of a catalytic oxidation system. We evaluated the effects of mixtures by comparing the destruction efficiencies for trichloroethylene in each test mixture (Table 2).

Table 2. Trichloroethylene Destruction Efficiency (%)

Mixture No.	Temperature (°F)			
	650	700	800	950
1	86	90	93	98
2	75	--	94	97
3	81	--	--	96
4	75	--	--	98

Mixture composition only affected destruction efficiency at a catalyst inlet temperature of 650°F. At this temperature, the trichloroethylene system destruction efficiency was significantly lower in Mixtures 2 and 4, than in Mixture 1. Although we observed an effect only at the lower temperatures, mixture effects have been reported at higher temperatures as well (Gangwal et al., 1986). The mechanism of such mixture interactions is not clear, therefore empirical laboratory or pilot-scale methods are the only techniques available at this time to provide an acceptable prediction.

Products of Incomplete Oxidation

Formation of new compounds due to incomplete oxidation is a major concern in any thermal destruction process--especially if the compounds of incomplete oxidation are also hazardous. No product of incomplete oxidation could be detected from Mixture 1. Traces of 1,1,1-trichloroethane (0.03 ppmv) and tetrachloroethylene (< 0.01 ppmv) were detected in effluent air during oxidation of Mixture 3, and effluent from oxidation of Mixture 4 contained 1,2-dichloroethylene (0.09 to 0.73 ppmv). CO emissions for all mixtures ranged from 5 to 170 ppmv. Concentrations decreased with increasing temperature and, at a given temperature, the CO concentration decreased with increasing air-to-gas ratio. Approximately 50% of the CO found in the incinerator outlet gas was from incomplete combustion of natural gas in the preheater flame.

HCl Formation

When the influent gas stream contains chlorinated compounds, the products of complete oxidation such as hydrochloric acid (HCl) may also be of concern. HCl concentrations and emission rates were calculated based on a catalyst inlet temperature of 800°F and a total inlet gas flow rate of 1,000 scfm. Predicted HCl concentrations for these operating conditions range from 6.3 to 28.1 ppmv. The corresponding HCl emission rates for a 1,000 scfm system range from 0.06 to 0.3 lb/hr. If these emission rates were unacceptable, some type of neutralization or scrubbing of the effluent would be required.

The tests we have described above are the minimum required to determine the effectiveness of catalytic oxidation for destroying VOCs in effluent from an air stripping operation. Although they provide information about the parameters of primary concern, they do not provide a complete picture. Humidity effects and catalyst life should also be considered.

UV-Catalytic Oxidizer

UV-Oxidizer Test Without Ozone

The highest destruction efficiency measured for tests without ozone was 64% at a space velocity of 200 hr^{-1}. Comparison of results for different test conditions indicates that the single most important parameter affecting the destruction efficiency for the UV system was space velocity (Table 3).

Table 3. UV-Catalytic Oxidizer Efficiency Without Ozone[a]

Compound	Inlet Concentration ppmv	Space Velocity hr^{-1}	Humidity Level (lb H_2O/ lb Dry Air)	Destruction Efficiency %
Dichloroethylene	5.99	3,000	Ambient	16
Trichloroethylene	3.82		(0.0133)	23
TOTAL	9.81			19
Dichloroethylene	6.43	800	Ambient	29
Trichloroethylene	4.12		(0.0138)	36
TOTAL	10.55			32
Dichloroethylene	5.18	800	High	30
Trichloroethylene	3.28		(0.0229)	44
TOTAL	8.46			35
Dichloroethylene	1.91	800	High	36
Trichloroethylene	0.95		(0.0144)	25
TOTAL	2.86			35
Dichloroethylene	1.80	200	High	67
Trichloroethylene	1.03		(0.0150)	59
TOTAL	2.83			64

[a]All tests conducted with a catalyst temperature between 80 and 96°F.

UV-Oxidizer Tests With Ozone

Destruction efficiencies for dichloroethylene and trichloroethylene were greater than 99% in the UV-catalytic system with ozone addition (Table 4). However, three unknown reaction products totaling approximately 2 ppmv (quantitated as trichloroethylene) were detected in the oxidizer outlet gas.

No chlorinated reaction products were found, but two nonchlorinated products were identified as methyl formate and methyl acetate. Total mixture destruction efficiency was approximately 75% for tests conducted at space velocities of 3,000 and 800 hr^{-1}.

Table 4. UV-Catalytic Oxidizer Efficiency with Ozone[a]

Compound (Retention Time) min	Inlet Concentration ppmv	Outlet Concentration ppmv	Destruction Efficiency %	UV Lights (On-Off)
Dichloroethylene	4.66	ND[b]	99+	On
Trichloroethylene	2.88	ND	99+	
Unknown (1.04)[c]	-	1.2	-	
Unknown (1.59)	-	0.36	-	
Unknown (1.90)	-	0.43		
Dichloroethylene	4.83	ND[b]	99+	On
Trichloroethylene	2.99	ND	99+	
Unknown (1.04)	-	1.0	-	
Unknown (1.59)	-	0.34	-	
Unknown (1.90)	-	0.52		
Dichloroethylene	4.83	ND[b]	99+	Off
Trichloroethylene	2.88	ND	99+	
Unknown (1.04)	-	1.1	-	
Unknown (1.59)	-	0.32	-	
Unknown (1.90)	-	0.60		

[a]All tests conducted with catalyst operating temperature of 88°F.
[b]ND = not detected at 0.03 ppmv detection limit.
[c]Unidentified compound quantitated as trichloroethylene. GC column retention given in parentheses.

CONCLUSIONS

Unreasonably long gas residence times are required for the UV-catalytic oxidizer to achieve acceptable destruction efficiencies of chlorinated hydrocarbon mixtures without ozone addition. Essentially complete destruction (99+%) of dichloroethylene and trichloroethylene can be achieved with ozone addition, but high concentrations of reaction products were formed.

Fluidized-bed catalytic incineration may be effective for the control of VOC emissions from air strippers. Destruction efficiencies from 97 to 99% are achievable for chlorinated organic mixtures with catalytic incineration. In contrast, Palazzolo, et al., 1985, observed catalyst destruction efficiencies of less than 50% for chlorinated organics on a platinum/paladium catalyst. The lower destruction efficiency can be attributed to a decrease in catalyst activity due to poisoning. Destruction efficiency is a strong function of catalyst inlet temperature and a weak

function of space velocity. Destruction efficiencies vary widely for different compounds.

Air stripping followed by catalytic oxidation of the off-gases can be a complete groundwater treatment system. The contaminants are destroyed rather than simply collected or concentrated prior to disposal. Further field studies are needed to determine catalyst life and effects of humidity on destruction efficiency. Laboratory studies are needed to provide a better understanding of the factors controlling catalytic oxidation of chlorinated organic/hydrocarbon mixtures. Once these questions are answered, a detailed cost analysis can be performed to determine the cost effectiveness of catalytic destruction techniques.

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Metric Equivalents - Readers more familiar with metric units may use the following equivalents to convert to that system:

Nonmetric	Times	Yields Metric
cfm	0.000472	m^3/s
^oF	5/9(^oF-32)	^oC
ft	0.305	m
ft^3	0.0283	m^3
in.	0.0254	m
$in.^3$	16.39	ml
lb/h	0.000126	kg/s